Probing the link between residual entropy and viscosity of molecular fluids and model potentials

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This work investigates the link between residual entropy and viscos-1 ity based on wide-ranging, highly-accurate experimental and sim-2 ulation data. This link was originally postulated by Rosenfeld in 3 1977, and it is shown that this scaling results in an approximately л monovariate relationship between residual entropy and reduced vis-5 cosity for a wide range of molecular fluids (argon, methane, CO₂, 6 SF₆, refrigerant R-134a (1,1,1,2-tetrafluoroethane), refrigerant R-125 (pentafluoroethane), methanol, and water), and a range of model 8 potentials (hard sphere, inverse power, Lennard-Jones, and Weeks-9 Chandler-Andersen). While the proposed "universal" correlation of 10 Rosenfeld is shown to be far from universal, when used with the ap-11 propriate density scaling for molecular fluids, the viscosity of non-12 13 associating molecular fluids can be mapped onto the model potentials. This mapping results in a length scale that is proportional to 14 the cube root of experimentally measureable liquid volume values. 15

viscosity | residual entropy | scaling

n 1977 Rosenfeld (1) postulated a quasi-universal relationship between reduced transport properties and the reduced residual entropy. This analysis was based on the analysis of simulation data for hard spheres, the one-component plasma, and the Lennard-Jones 12-6 model potential in the *liquid phase only*. This scaling, here referred to as the *Rosenfeld scaling*, was of the form

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$$\frac{\eta}{\eta^{\rm R}} = f\left(-\frac{s^{\rm r}}{R}\right),\tag{1}$$

⁹ where the reducing viscosity $\eta^{\rm R}$, in the same units as η , is ¹⁰ given by

$$\eta^{\rm R} = \rho_{\rm N}^{2/3} \sqrt{mk_{\rm B}T},\qquad[2]$$

which is obtained by scaling the viscosity in units of Pa·s (with 12 dimensions of mass/(length×time)) by the appropriate dimen-13 sional scaling parameters (for Newtonian dynamics, mass: m, time: $\rho_{\rm N}^{-1/3} \sqrt{m/(k_{\rm B}T)}$, length: $\rho_{\rm N}^{-1/3}$)(2, 3). The parameter $\rho_{\rm N}$ is the number density, not to be confused with the molar 14 15 16 density ρ , m is the mass of one particle or molecule in kg, $k_{\rm B}$ 17 is the Boltzmann constant in $J \mod^{-1}$, T is the temperature 18 in kelvins, and $-s^{r}/R$ is the reduced residual entropy. For 19 more on the selected unit system and nomenclature, see the 20 supporting information (SI) appendix in Section ??. 21

Twenty-two years later, in 1999, Rosenfeld (4) proposed
the "universal" correlation for viscosity given by

$$\frac{\eta}{\eta^{\mathrm{R}}} = 0.2 \exp\left(-0.8\frac{s^{\mathrm{r}}}{R}\right).$$
[3]

Empirical equations of a similar form have been obtained for a growing body of fluids and intermolecular potentials in dense phases(5–9).

Over the last few years, a theoretical basis for the scaling effects that Rosenfeld saw four decades ago has been developed with isomorph theory(2, 3, 10–14). This theory stipulates that the viscosity scaled in the manner of Eq. (1) should be 31 invariant along lines of constant residual entropy if there is a 32 high degree of correlation between fluctuations in the virial 33 of the system and fluctuations in its intermolecular potential 34 energy. A fluid that follows this behavior, even in *some* of its 35 phase space, is referred to as an R-simple (Roskilde simple) 36 fluid (3). No molecular fluids are truly perfectly correlating 37 in the R-simple sense, and furthermore, this R-simple scaling 38 may only apply in part of the liquid domain, but this is a 39 powerful theoretical tool to understand the dynamic behavior 40 of molecular fluids. The recent review of Dyre (14) summarizes 41 the state-of-the-art in residual entropy scaling of transport 42 properties. 43

Density scaling and residual entropy scaling are directly connected by isomorph theory (15–20). The reduced dynamic properties of fluids that can be modeled with inverse-power pair potentials scale with $\rho^{n/3}/T$ where *n* is the exponent of the inverse-power pair potential (15, 19, 20); for the inversepower pair potential (see Section B), there is a one-to-one relationship between $\rho^{n/3}/T$ and the residual entropy (see SI Appendix, Fig. ??).

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Rosenfeld scaling can also be applied to dynamic properties 52 like diffusivity; there are now a number of studies focused on 53 Rosenfeld scaling of diffusivity from molecular simulation (see 54 for instance (21-26)) due to the ease with which self-diffusion 55 can be extracted from the results of molecular simulations. 56 Studies considering the entropy scaling of experimental diffu-57 sivity measurements are growing in number as well (25, 27–29). 58 As is highlighted by (25, 27), and also seen in this work in 59 the case of viscosity, one of the limitations of the Rosenfeld 60 scaling applied to self-diffusion is that unique curves are in 61 general obtained for each species studied. The residual entropy 62 corresponding states approach proposed in this work should 63 also apply to self-diffusion, allowing for harmonization of the 64 self-diffusion studies that have been carried out thus far. 65

The Rosenfeld scaling of viscosity has been comparatively 66

Significance Statement

We confirm, based on a large database of experimental measurements, Rosenfeld's hypothesis from 1977 that the viscosity (a transport property) and the residual entropy (a thermodynamic property) are intimately connected in dense fluid phases. This study also provides a means to estimate viscosity with knowledge of only thermodynamic property information, or to characterize a fluid's full liquid viscosity surface based upon a very small number of high-accuracy experimental measurements. less studied. Abramson(30-35) was one of the first to consider
the Rosenfeld scaling of his experimental viscosity data at
very high pressures. Since then, modified Rosenfeld scaling
of viscosity (reducing by the dilute-gas viscosity rather than

Eq. (2) has also been successfully investigated (36-42).

This work investigates the hypothesis that the Rosenfeld-72 scaled viscosity should in general be invariant along lines of 73 74 residual entropy, as is proposed by isomorph theory. The most comprehensive study to date of this hypothesis based 75 upon viscosities obtained from experimental measurements of 76 molecular fluids and molecular simulation of model potentials 77 is carried out here. The nearly monovariate relationship for 78 non-associating fluids between reduced viscosity and residual 79 entropy in the liquid phase, where simple fluids are approx-80 imately R-simple, is shown. Furthermore, this monovariate 81 scaling is shown to apply surprisingly well to hydrogen-bonding 82 fluids approaching the melting line. Network forming (hydro-83 gen bonding) tends to destroy the R-simple character of the 84 85 fluid and is expected to result in a non-monovariate scaling between reduced viscosity and residual entropy. 86

The model potentials show the same monovariate depen-87 88 dency of reduced viscosity on the residual entropy as the 89 molecular fluids, and deviate from this behavior in the same ways. The scaling of the molecular fluids and the model po-90 tentials collapse by a residual entropy corresponding states 91 approach. In this case, the residual entropy (the measure of 92 structure of the fluid phase) is the parameter that must be 93 corresponding for dynamic states to be equivalent. 94

Thermodynamic and transport properties have traditionally been considered independently. This work shows that: *Residual entropy is the scaling parameter that connects the thermodynamic and transport properties of dense fluids.*

While empirical viscosity models are usually complicated 99 functions of temperature and density (43, 44), much simpler 100 functional forms can be developed in terms of one variable, the 101 residual entropy. This scheme offers the practical promise of a 102 different approach for correlating the viscosity of fluids. Only 103 a single variable (the residual entropy) is involved, and thus far 104 fewer experimental data points would be required compared 105 to a function depending on temperature and density. We have 106 begun to apply residual entropy scaling with promising results. 107

108 1. Molecular fluids

The term "molecular fluid" is used in this work to differentiate
from model intermolecular potentials; model potentials are
useful theoretical models but are not experimentally accessible
in a laboratory. The study of molecular fluids in this section is
indebted to the work of the experimental transport property
community; without their tireless work, this study would not
have been possible.

A. Fluid selection. Molecular fluids for this study were selected
 according to the availability of:

- a significant body of high-quality experimental viscosity
 data covering most of the liquid, gas, and supercritical
 states, and
- a well-constructed equation of state for the thermodynamic properties that yields high-fidelity predictions of
 the residual entropy over the entire fluid range.

Unfortunately, there are not many fluids (perhaps 30) that meet these requirements. The selected molecular fluids represent the following classes:

- a monatomic gas (argon), 127
 nonpolar molecules (methane, carbon dioxide, and sulfur hexafluoride), 129
- halogenated refrigerants (R-134a and R-125) with electrostatic interactions due to polarity, and

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• strongly associating fluids (methanol and water)

Table 1 lists the equations of state that were employed in
this work. All of the equations of state are multiparameter
reference equations. The NIST REFPROP thermophysical
property library (45) was used to carry out all the calculations.133The equations of state in REFPROP have been critically
assessed and deemed to be the most reliable for the given fluid
and all have been published in the literature.133

Table 1. Equations of state used in this work

Common name	EOS	$T_{ m max}$ (K)	$p_{ m max}$ (MPa)	
Argon	(46)	2000	1000	
Methane	(47)	625	1000	
SF ₆	(48)	625	150	
CO_2	(<mark>49</mark>) ^a	2000	800	
R-134a	(<mark>50</mark>)	455	70	
R-125	(<mark>51</mark>)	500	60	
Methanol	(<mark>52</mark>)	620	800	
Water	(<mark>53</mark>)	2000	1000	

a: The equation of state of Giordano *et al.* (54) is used above 800 MPa instead of that of Span and Wagner(49).

If temperature and pressure are known for the experimental 140 state point, the density is iteratively obtained from the equa-141 tion of state. With the exception of carbon dioxide, for which 142 the equation of state of (54) (see SI Appendix, Section ?? for 143 the use of this EOS) was used above the maximum pressure 144 of the equation of state of (49), measurements at pressures 145 above the stated maximum pressure of the EOS were excluded 146 to avoid errors associated with extrapolation. 147

In the SI Appendix, Fig. ?? shows the coverage of the experimental viscosity data available for the studied fluids, and the limits of the equations of state for these fluids. This figure demonstrates that there is significant disparity in data coverage, even among the best-studied fluids.

B. Evaluation of s^{r} . The state-of-the-art equations of state for molecular fluids are Helmholtz-energy explicit with temperature and density as independent variables. In these formulations, the molar Helmholtz energy a is expressed as a sum of the ideal-gas $a^{0} = RT\alpha^{0}$ and residual $a^{r} = RT\alpha^{r}$ contributions, given as

$$\alpha(\tau,\delta) = \frac{a}{RT} = \alpha^{0}(\tau,\delta) + \alpha^{r}(\tau,\delta), \qquad [4] \quad {}_{156}$$

where the independent variables are the reciprocal reduced temperature $\tau = T_{\rm c}/T$ and the reduced density $\delta = \rho/\rho_{\rm c}$, 161 and $T_{\rm c}$ and $\rho_{\rm c}$ are the critical temperature and molar density, 162 respectively. 163 Expressed in terms of derivatives of α , the molar entropy 165 $s = -(\partial a/\partial T)_{\rho}$ is given by

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$$\frac{s}{R} = \tau \left[\left(\frac{\partial \alpha^0}{\partial \tau} \right)_{\delta} + \left(\frac{\partial \alpha^r}{\partial \tau} \right)_{\delta} \right] - \alpha^0 - \alpha^r.$$
 [5]

and the residual entropy $s^{\rm r}$ is the part of Eq. (5) that is based only on $\alpha^{\rm r}$ and its derivatives, resulting in

$$\frac{s^{\rm r}}{R} = \tau \left(\frac{\partial \alpha^{\rm r}}{\partial \tau}\right)_{\delta} - \alpha^{\rm r}.$$
 [6]

For additional details of the use of multiparameter EOS, the reader is directed to the literature (55–57).

The residual entropy should not be confused with the term "excess" entropy (27, 58), which refers to differences of mixture thermodynamics from ideal-solution behavior.

The residual entropy is defined as the part of the entropy 175 that arises from the interactions among particles or molecules. 176 This contribution is negative due to repulsive and attractive 177 interactions that increase the structure beyond that of the 178 non-interacting ideal gas(19). To illustrate this property, Fig. 1 179 shows contours of the reduced residual entropy for ordinary 180 water, where $-s^{\rm r}/R$ is evaluated from the equation of state 181 of Wagner and Pruß (53). In the zero-density limit, $-s^{\rm r}/R$ 182 is zero (no increase in structure caused by molecular inter-183 actions), and as the density increases, so does $-s^{\rm r}/R$. The 184 maximum value for $-s^{r}/R$ is found along the melting line at 185 the maximum pressure of the equation of state; this can be 186 intuitively understood as the state within the fluid domain 187 where the fluid is most structured. 188



Fig. 1. Contours of the residual entropy s^r/R for water from the equation of state of Wagner and Pruß (53). The dashed curve is the line of maximum pressure of the equation of state, the solid red curve is the melting curve, and the solid black curve is the vapor-liquid co-existence curve (the binodal).

C. Data Analysis. Experimental viscosity data were curated for 189 a selection of fluids that experience more complex interactions 190 191 than the simple model fluids investigated by Rosenfeld(1). For each experimental data point, the molar density was 192 determined, either taken directly from the measurement or 193 from an iterative thermodynamic calculation of the equation of 194 state given T and p. The residual entropy was then evaluated 195 at the specified molar density and temperature as described 196 in Section **B**. 197

Figure 2 shows the experimental viscosity data for the eight molecular fluids under study, with the Rosenfeld "universal" relationship overlaid for each fluid. The viscosity is reduced in the same manner as proposed by Rosenfeld (1). The data for each of the fluids in these scaled coordinates has a characteristic, and roughly similar, shape. The data for other molecular fluids (investigated but not discussed in this paper) also have the same shape. 205

For the fluids that are Lennard-Jones-like (e.g., argon or 206 methane), the "universal" correlation of Rosenfeld captures 207 the correct qualitative relationship between the viscosity and 208 the residual entropy at liquid-like conditions $(-s^r/R \ge 1)$ at 209 moderate densities. As the intermolecular interactions quali-210 tatively increase in intensity (i.e., for the associating fluids), 211 the Rosenfeld "universal" relationship does not agree with the 212 experimental data either qualitatively or quantitatively in the 213 liquid-like phase. 214

Costigliola et al. (59) and others (19, 60, 61) suggest 215 that water (and other associating fluids) should not have a 216 monovariate viscosity scaling in terms of residual entropy in 217 the liquid phase due to the presence of hydrogen-bonding 218 networks. Fig. 2 shows that water does in fact demonstrate 219 an approximate collapse of the reduced viscosity surface with 220 monovariate dependency on the reduced residual entropy, with 221 the exception of states approaching the melting line where 222 the analysis of Ruppeiner and co-authors (see Section C.1) 223 suggests a means of identifying the presence of hydrogen-224 bonding networks from a high accuracy equation of state. 225

C.1. Liquids. For liquid-like states $(-s^r/R \ge 1)$, the experimen-226 tal data for each non-associating molecular fluid (aside from 227 some scatter in the experimental measurements) collapse onto 228 master curves – a monovariate functional dependence. The 229 curvature in semi-log coordinates differs depending on the in-230 termolecular interactions. In the case of argon, methane, SF_6 , 231 CO_2 , and the refrigerants R-134a and R-125, the liquid-like 232 scaling is roughly linear in semi-log coordinates. The exper-233 imental data for these fluids (particularly for SF_6 and CO_2) 234 and less so for R-134a and R-125) extend to the melting line 235 (SI Appendix, Fig. ??). 236

For the associating fluids methanol and water, a more 237 complicated functional dependence is seen, particularly at 238 large values of $-s^{\rm r}/R$. While the reduced viscosity data are 239 still a nearly monovariate function of the residual entropy, 240 the curvature of the data increases at higher values of $-s^{\rm r}/R$. 241 The pronounced increase in curvature can be ascribed to the 242 presence of transient structures in the fluid caused by hydrogen-243 bonding networks in the bulk liquid phase. This pronounced 244 curvature in the Rosenfeld-scaled viscosity is consistent with 245 the behavior identified by other authors for diffusivity (25) and 246 viscosity(34) of water. The thermodynamic states where these 247 networks are present can be identified by states with positive 248 Riemannian curvature (62-65). 249

To assess the monovariability of the relationship between the reduced viscosity and the residual entropy, polynomial correlations for each fluid at states from $-s^{\rm r}/R = 0.5$ up to the melting curve of the fluid were developed in this work. The correlations are of the form 254

$$\ln\left[\frac{\eta}{\rho_{\rm N}^{2/3}\sqrt{mk_{\rm B}T}}\cdot\left(-\frac{s^{\rm r}}{R}\right)^{2/3}\right] = \sum_{i}c_{i}\left(-\frac{s^{\rm r}}{R}\right)^{i}.$$
 [7] 255

Multiplication of the reduced viscosity by $(-s^r/R)^{2/3}$ was used to remove the divergence in the dilute-gas limit, consistent 257



Fig. 2. Overview of relationship between reduced viscosity and residual entropy for the molecular fluids from a total of 12987 experimental data points. The dashed line represents the "universal" scaling law of Rosenfeld (4). The data are vertically stacked by multiplying by increasing powers of 10.

with the theory of Rosenfeld (4, 14) that the reduced viscosity 258 should be proportional to $(-s^r/R)^{-2/3}$ in dilute gases. The 259 coefficients of the polynomial fits are in the SI Appendix (Table 260 ??). Figure 3 shows the deviations between the experimental 261 data points and calculations from the fits from Eq. (7). Even 262 though the absolute deviations are as much as 35 % for the 263 hydrogen-bonding fluids in the compressed liquid due to the 264 breakdown in monovariability caused by hydrogen bonding, 265 the average absolute deviation (AAD) for each fluid is less 266 than 4.3% for $-s^{\rm r}/R > 0.5$. This demonstrates that the 267 relationship between reduced viscosity and residual entropy is 268 indeed approximately monovariate (except for the associating 269 fluids). 270

The practical implication of this is that if an equation of state of sufficient accuracy is available for a fluid, a correlation of viscosity in terms of residual entropy can describe the viscosity surface.

These liquid-like data do not directly refute the analysis of 275 Rosenfeld, who merely proposed a monovariate relationship 276 between reduced viscosity and residual entropy. The results in 277 Fig. 2 and Fig. 3 indicate that this monovariate relationship 278 is present, even if the relationship might be different for each 279 fluid. As shown in Section 3, the mapping onto the results of 280 model intermolecular potentials can reduce the data so that 281 non-associating fluids can all be collapsed onto a single curve 282 with one adjustable parameter. 283

C.2. Gas. In the gaseous domain where $-s^r/R \lesssim 1$, there is a pronounced deviation from monovariate scaling, as is visible

in Fig. 2, and more readily seen in the detailed view of this region in the SI Appendix (Fig. ??). This figure demonstrates two deficiencies in the scaling proposed by Rosenfeld:

- The scaling diverges at zero density (where $-s^{\rm r}/R=0$). 285
- The gaseous region does not reduce to a monovariate dependence of reduced viscosity with $-s^{\rm r}/R$.

Other authors (36-42, 66) have proposed alternative 292 residual-entropy-based schemes that are more successful at 293 scaling the viscosity in the dilute gas limit, but they intro-294 duce significant deviations from monovariate scaling in the 295 compressed liquid phase for small non-associating molecules 296 and in the gaseous phase for associating molecules. Exam-297 ples of these difficulties for argon and water are shown in the 298 SI Appendix (Fig. ??). For that reason alternative entropy 299 scalings are not discussed in this work; further work will in-300 vestigate potential means of reconciling these different scaling 301 approaches. 302

Isomorph theory describes *why* the reduced viscosity should 303 not be a monovariate function of the residual entropy in the 304 gas phase. In this region, the motion of the molecules is 305 predominantly ballistic, aside from the infrequent interactions 306 between molecules via collision. Therefore, the fluid should not 307 be R-simple, isomorph scaling should be invalid, and reduced 308 viscosity should not be a monovariate function of residual 309 entropy. 310



Fig. 3. Deviations from monovariability between data and fits from Eq. (7). The deviation term is given by $\Delta\eta=100\times(\eta_{\rm fit}/\eta_{\rm exp}-1)$ and dashed lines represent $\pm10\%$. The correlation is fit for $-s^{\rm r}/R>0.5$; values below the range of the fit are impacted by the extrapolation behavior of the fit and non-monovariate scaling.

311 2. Model potentials

Model intermolecular potentials, and the simulation results 312 that are obtained from these potentials, have much to teach 313 us about transport properties of molecular fluids. After some 314 general information, this section covers four model potentials. 315 The viscosity of single-site models in molecular simulations 316 is in general given in the form $\eta^* = \eta \sigma^2 / \sqrt{m\varepsilon}$ (67), in terms of 317 the reduced temperature $T^* = T/(\varepsilon/k_{\rm B})$ and reduced density 318 $\rho^*=\rho_{\rm N}\sigma^3,$ where ε is an energy scale, σ is a length scale, and 319 $\rho_{\rm N}$ is the number density in m⁻³; for more information on 320 working in molecular simulation units, see (68). 321

A. Hard sphere. The hard sphere model potential is a par-322 ticularly simple one; rigid spherical particles have ballistic 323 trajectories until they collide with another particle. The re-324 duced viscosity of the hard-sphere potential, as well as its 325 associated residual entropy, can each be obtained as a function 326 of the packing fraction $\zeta = \pi \rho^*/6$. The parameter ζ is not a 327 function of temperature, but only a function of density. In 328 the SI Appendix (Fig. ??) is a graphical representation of 329 the scaling for the hard sphere, and the curve of the reduced 330 viscosity versus the residual entropy is also shown in Fig. 4. 331 The shape of the viscosity versus $-s^{r}/R$ curve in scaled coor-332

B. Inverse-power pair potential. Real molecules are not rigid; 340 they are more like a rubber ball than a billiard ball. As a 341 result, it is more reasonable to treat molecules as soft spheres 342 than hard spheres. The inverse-power pair potential (IPP) 343 is a repulsive potential commonly used to model fluids with 344 soft repulsive interactions given by $U = \varepsilon (\sigma/r)^n$, where r is 345 the radius in meters and n is an integer power. The density 346 and temperature are not independent for the IPP potential 347 (11, 72, 73); they are linked via the scaling variable $\gamma =$ 348 $\rho_{\rm N}\sigma^3 (T^*)^{-3/n}$. 349

The ratio of viscosity η to $\rho_{\rm N}^{2/3} \sqrt{mk_{\rm B}T}$ is then

$$\frac{\eta}{\rho_{\rm N}^{2/3}\sqrt{mk_{\rm B}T}} = \frac{\eta^*/(T^*)^{n'}}{\gamma^{2/3}},$$
[8] 351

in which n' = (2/n) + (1/2). The simulation for the IPP 352 potential is carried out at specified pairs of $\rho^* = \rho_N \sigma^3$ and 353 $T^* = Tk_{\rm B}/\varepsilon$, for which the simulation data are expressed in 354 terms of $\eta^*/(T^*)^{n'}$ as a function of the scaling variable γ (see 355 (74) and the SI Appendix (Section ??)). For the n = 12 IPP 356 potential, the residual entropy is obtained from integration 357 of the convergent virial expansion given by (72). For other 358 values of n, the asymptotically convergent approximation of 359 (73) is used (SI Appendix, Section ?? for further description 360 of this method). 361

C. Lennard-Jones. Real fluids interact by both attraction and repulsion (as well as long-range electrostatic interactions); the potential should capture this. The canonical example of a fluid with both attraction and repulsion is the Lennard-Jones 12-6 potential; it is given by

$$U = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right].$$
 [9] 367

A number of researchers have carried out molecular sim-368 ulation on the Lennard-Jones 12-6 potential, and evaluated 369 viscosities through application of the Green-Kubo formalism 370 (75). The coverage of the simulation results for the Lennard-371 Jones fluid is shown in the SI Appendix (Fig. ??). The most 372 accurate equation of state for the Lennard-Jones 12-6 potential 373 is the one recently developed by Thol et al. (76), which is 374 valid up to $T^* = 9$ and $p^* = 65$, where $p^* = p\sigma^3/\varepsilon$. Due to the 375 availability of the multiparameter EOS for the Lennard-Jones 376 12-6 potential(76), the same methodology for the Lennard-377 Jones 12-6 potential is applied as with the molecular fluids in 378 Section B – for a given set of T^* , ρ^* , and η^* from one simu-379 lation, the residual entropy is evaluated from the equation of 380 state as described in Eq. (6). 381

D. WCA. Weeks, Chandler, and Andersen (WCA) (77) proposed a means of deconstructing potentials into reference and attractive contributions. The reference part of the WCA deconstruction of the Lennard-Jones 12-6 potential results in a fully repulsive potential that has dynamic behavior similar to

that of the Lennard-Jones 12-6 potential with shorter-ranged 387 interactions. This reference potential is obtained by truncat-388 ing the Lennard-Jones 12-6 potential at the location of its 389 minimum value at $r = 2^{1/6} \sigma$ and shifting the curve upwards 390 391 by ε , or

$$U = \begin{cases} 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] + \varepsilon, & r \le 2^{1/6}\sigma \\ 0, & r > 2^{1/6}\sigma. \end{cases}$$
[10]

We refer to the reference part of the WCA deconstruction 393 of the Lennard-Jones 12-6 potential as the "repulsive WCA 394 potential" for concision. 395

The repulsive WCA potential retains the same intermolecu-396 lar force between molecules as the Lennard-Jones 12-6 potential 397 (the force between particles is the negative of the derivative 398 of the potential with respect to position) within $r < 2^{1/6}\sigma$. 399 The transport properties of the repulsive WCA potential are 400 similar to those of the Lennard-Jones 12-6 potential, while 401 having thermodynamic properties that are more straightfor-402 ward to evaluate because the equation of state reduces to a 403 quasi-monovariate function of the effective packing fraction 404 without a liquid phase or a critical point (78). 405

Analogously to the soft-sphere potential, an effective pack-406 ing fraction (with implicit temperature dependence) is defined 407 by Heyes and Okumara (79) by $\zeta_{\rm e} = \pi \rho^* \left(\sigma_{\rm e} / \sigma \right)^3 / 6$, with the 408 effective particle diameter given by $\sigma_{\rm e}/\sigma = [2/(1+\sqrt{T^*})]^{1/6}$. 409 Alternative effective particle diameter models are described in 410 the literature (80-83). The residual entropy of the repulsive 411 WCA potential is obtained by integration of the empirical com-412 pressibility factor model proposed by Heyes and Okumara (79) 413 (see SI Appendix, Section ??). There is currently a scarcity of 414 high-accuracy tabulated viscosity data for the repulsive WCA 415 potential; however, sufficient data exist to develop the empiri-416 cal correlation given in the SI Appendix. Of particular interest 417 are the new simulation results from Krekelberg provided in 418 the SI Appendix (Section ??) with permission. 419

E. Overview. Figure 4 presents the simulation results for all 420 the model potentials included in our study. These data com-421 prise the corpus of data for the Lennard-Jones 12-6 potential, 422 simulation results for the IPP with n = 12, results for the 423 repulsive WCA potential, and the curve for the hard-sphere 424 potential. 425

The "universal" scaling of Rosenfeld does not reproduce all 426 of the Lennard-Jones simulation data in the liquid phase. In 427 the work of Rosenfeld (4), he described good agreement with 428 simulation results for the "universal" correlation. In reality, the 429 correlation was compared with a single data set comprising four 430 data points at zero shear rate from Ashurst and Hoover (84, 431 Table VI); the present data coverage of results on the Lennard-432 Jones fluid here is far more comprehensive. Rosenfeld's curve 433 of "universal" scaling might not have been quite right, but with 434 the appropriate caveats, most repulsive-dominated potentials 435 are remarkably consistent in the Rosenfeld scaling framework. 436

3. Residual Entropy Corresponding States 437

Figures 2 and 4 demonstrate a remarkable similarity for the 438 non-associating fluids. The primary difference between fluids 439 and potentials is the scaling of the residual entropy. Therefore, 440 a means of connecting the molecular fluids and the model 441



Fig. 4. Overlaid data for each of the model potentials studied in this work (blue \triangle : Lennard-Jones 12-6 potential (67, 85–90); black \triangleleft : IPP with n = 12 (74); red \bigcirc : repulsive WCA potential: vellow \triangle : Lennard-Jones data from Ashurst and Hoover(84) (zero-shear-rate extrapolation) considered by Rosenfeld (1); orange dashed curve: hard sphere (Enskog theory plus correction of (91)); black dashed line; correlation from Rosenfeld(4)). A larger version of this figure is available in the SI Appendix (Fig. ??).

potentials is needed. This link is formed through the use of residual entropy corresponding states.

It is possible to map from experimental units into simulation 444 units of T^* , ρ^* , etc. by adjusting the parameters $\varepsilon/k_{\rm B}$ and σ . 445 Carrying out the appropriate cancellation results in 446

$$\frac{\eta}{\rho_{\rm N}^{2/3}\sqrt{mk_{\rm B}T}} = \frac{\eta^*}{\left(\rho^*\right)^{2/3}\sqrt{T^*}}$$
[11] 447

and, therefore, scaling properties from number density to ρ^* , 448 from temperature to T^* , and from viscosity to η^* will not 449 change the Rosenfeld-reduced viscosity. On the other hand, 450 modifying $\varepsilon/k_{\rm B}$ and σ adjust the residual entropy. 451 452

At this point, it is necessary to determine:

- the most appropriate reference potential, and
- a set of values for σ for the mapping from a molecular 454 fluid to a reference potential

While the Lennard-Jones potential is appealing as a model 456 potential, its use as the reference system for molecular fluids 457 is problematic because 458

- the Lennard-Jones 12-6 potential behaves like a molecular fluid and has a liquid phase (see the relevant phase diagrams in the SI Appendix, Fig. ??, and Fig. ??), and also no convenient scaling variable such as the γ of the IPP potential,
- the equation of state for the Lennard-Jones 12-6 potential 464 has areas in the unstable region between the spinodals 465 where non-physical residual entropies are obtained (see 466 the SI Appendix, Fig. ??), and 467
- no highly accurate viscosity correlation for the Lennard-468 Jones 12-6 potential exists, though several empirical vis-469 cosity correlations of poorer accuracy are available in the 470 literature (92, 93). 471

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Table 2. Optimized values of σ for the eight molecular fluids included in this study. Units of all variables are 10^{-10} m (Å)

fluid	$v_{\rm N,triple}^{1/3}$	$v_{{\rm N},0.8{\rm T_c}}^{1/3}$	$v_{\rm N,crit}^{1/3}$	σ_{IPP}	$\sigma_{ m WCA}$
Water	3.104	3.334	4.529	3.084	2.973
Argon	3.615	3.855	4.985	3.676	3.476
CO_2	3.966	4.081	5.387	3.943	3.724
Methane	3.901	4.226	5.471	3.957	3.733
Methanol	3.892	4.311	5.739	4.178	3.950
R-134a	4.745	5.204	6.917	5.095	4.830
SF_6	5.094	5.250	6.888	5.244	4.995
R-125	4.909	5.314	7.030	5.265	4.992

For these reasons, scaling onto the repulsive WCA potential 472 was chosen; the repulsive WCA potential has a compressibility 473 factor that is a monovariate function of the thermodynamic 474 scaling parameter $\zeta_{\rm e}$, and the simulation results for the vis-475 cosity of the repulsive WCA potential lie within the range of 476 results from the Lennard-Jones simulations (see Fig. 4). Map-477 ping the properties onto the n = 12 IPP potential was slightly 478 479 less successful, as described in the SI Appendix (Fig. ??). The mapping onto the hard-sphere potential was also carried out 480 with the same methodology. The hard-sphere mapping was 481 not successful, as is shown in the SI Appendix (Fig. ??). 482

The value of $\varepsilon/k_{\rm B}$ was set equal to the critical temperature 483 of the molecular fluid divided by 1.32 ($T_{\rm c}^*$ = 1.32 for the 484 Lennard-Jones equation of state (76); the repulsive WCA 485 potential is fully repulsive and therefore does not have a critical 486 point) and σ was left as an adjustable parameter. In this 487 way, corresponding states between the Lennard-Jones analog 488 (the repulsive WCA potential) and the molecular fluid are 489 enforced. Values of $\varepsilon/k_{\rm B} = T_{\rm c}$ and $\varepsilon/k_{\rm B} = T_{\rm c}/0.7$ were also 490 considered, as described in the SI Appendix; there is a very 491 weak dependence of σ on $\varepsilon/k_{\rm B}$. 492

Each fluid was mapped onto the residual entropy of the reference potential. In order to do this, a one-dimensional optimization of σ was carried out to minimize the difference between the Rosenfeld scalings at liquid-like states. The approach is as follows:

- ⁴⁹⁸ 1. For a given molecular fluid experimental datapoint ⁴⁹⁹ for which $-s^{\rm r}/R > 1$, calculate the reduced quantity ⁵⁰⁰ $\eta/[\rho_{\rm N}^{2/3}\sqrt{mk_{\rm B}T}].$
- 2. At the same value of reduced viscosity for the repulsive WCA correlation, calculate the corresponding value of ζ_{e} for the repulsive WCA potential; the correlation is monotonic.
- 3. From $\zeta_{\rm e}$, calculate ρ^* for the given $\sigma_{\rm e}/\sigma$ from $\rho^* = 6\zeta_{\rm e}(\sigma_{\rm e}/\sigma)^3/\pi$, and then obtain $\sigma = (\rho^*/\rho_{\rm N})^{1/3}$.

The median value of σ among all the experimental data points 507 for which a value of σ is successfully obtained is retained; the 508 median σ was used in order to avoid the influence of outliers. It 509 may not be possible to obtain the value for σ if $\eta/[\rho_N^{2/3}\sqrt{mk_BT}]$ is below the minimum value of $\eta/[\rho_N^{2/3}\sqrt{mk_BT}] \approx 0.57$ that can be achieved for the repulsive WCA potential. Once the 510 511 512 value of σ has been determined for a molecular fluid, this value 513 can then be used to scale all the experimental data into the 514 'simulation" units of T^* , ρ^* , η^* . 515

This approach was carried out for the eight molecular fluids discussed in this study, and the obtained values of σ are given



Fig. 5. Scaled experimental data mapped onto the repulsive WCA potential for the non-associating fluids argon, methane, CO₂, SF₆, R-134a, and R-125. The residual entropies are evaluated for the repulsive WCA potential. The solid line is the correlation for the repulsive WCA potential, and the dashed lines show $\pm 20\%$.

in Table 2. Figure 5 shows the scaled experimental data for 518 the non-associating fluids; the results for associating fluids 519 are shown in the SI Appendix (Fig. ??). In the case of the 520 non-associating fluids, the qualitative agreement is surprisingly 521 good; with the appropriate scaling, all experimental data can 522 be closely mapped onto a master curve given by the repulsive 523 WCA correlation. The repulsive WCA model potential does 524 not perfectly match the Rosenfeld-scaled experimental data 525 mapped onto the repulsive WCA potential, and it is evident 526 that although the majority of the data in the liquid phase can 527 be predicted within 20% (the dashed lines), the curvature of 528 the mapped experimental data does not perfectly match the 529 curvature of the correlation. 530

Figure 6 shows the deviations between the experimental 531 viscosities and the viscosities calculated by the fitted values 532 of σ for each of the non-associating fluids described in Fig. 5. 533 Within the recommended range of validity $(0.5 \leq -s^r/R \leq 3.5)$ 534 of the repulsive WCA potential, the deviations are in general 535 less than 10% within the bulk of the range, except at larger 536 values of $-s^{\rm r}/R$, where the curvature of the repulsive WCA 537 potential results begins to move the correlation away from the 538 experimental data (see Fig. 5). Within the center of the region 539 of validity, the absolute deviations are in general less than 5%. 540

The same exercise was made for all the molecular fluids 541 that a) have a Helmholtz-energy explicit equation of state 542 available in the NIST REFPROP thermophysical property 543 library (45) and b) have experimental liquid viscosity data 544 available in the NIST ThermoData Engine version 10.1 (94). 545 The fluids included in this suite include hydrocarbons, refrig-546 erants, siloxanes, noble gases, fatty-acid methyl esters, etc. 547 In total, 120 fluids were included in the analysis, with molar 548 masses ranging from 2 g mol⁻¹ (hydrogen) to 459 g mol⁻¹ 549 $(MD_4M).$ 550

The fitted values for σ are shown in Fig. 7 as a function of three characteristic volumes, those at the critical point, the liquid at the triple point, and the saturated liquid at $0.8T_c$. The fact that σ^3 should be proportional to the critical volume was originally proposed in corresponding states theory (28, 95), and these data confirm this proposition. A similar linear rela-

tionship between the cube root of the critical volume and the 557 length scale was seen by Liu et al. (28) with diffusivity data. It 558 is remarkable that this behavior holds even for fluids that are 559 associating (ethanol, water, etc.), for which this relationship is 560 561 not expected to be followed. The proportionality constant of 562 the critical point volume scaling is approximately 0.7, which is quite different than the value given by the Chung model 563 for extended corresponding states (96, 97) of 0.958. An even 564 more remarkable relationship is found when the length-scaling 565 parameter is plotted against cube root of the volume of the 566 liquid at the triple point; the length scaling parameter is approximately equal to $v_{N,triple}^{1/3}$. We currently have no theoretical 567 568 explanation for this behavior. A third length scale based on 569 the cube root of the volume of the saturated liquid at $0.8T_{\rm c}$ 570 also results in a nearly linear functional dependence; this is a 571 more meaningful liquid corresponding states point than the 572 triple point because the latter depends on solid-phase prop-573 erties. In the SI Appendix (Section ??) additional candidate 574 length scales are further described, including the length scale 575 obtained from Noro-Frenkel universalism (98) and the length 576 scales obtained for $\varepsilon/k_{\rm B} = T_{\rm c}$ and $\varepsilon/k_{\rm B} = T_{\rm c}/0.7$ for each 577 reference potential. 578



Fig. 6. Deviations between Rosenfeld-scaled experimental data mapped onto the repulsive WCA potential and experimental data for the non-associating fluids argon, methane, CO₂, SF₆, R-134a, and R-125. Absolute deviations are given by $|\Delta \eta| = |(\eta_{\rm fit}/\eta_{\rm exp}-1) \times 100|$. The colored rectangle is the approximate range of validity of this method, and the dashed line indicates 10%

⁵⁷⁹ While the mapping between experimental data and model ⁵⁸⁰ potentials via the residual entropy is fruitful, one challenge ⁵⁸¹ is that the repulsive model potentials reach their respective ⁵⁸² solid-liquid-equilibrium curve at smaller values of $-s^r/R$ than



Fig. 7. Optimized values of σ for each fluid for the mapping to the repulsive WCA reference potential for $\varepsilon/k_{\rm B}=T_{\rm c}/1.32$. The slightly transparent markers correspond to the full set of fluids from NIST REFPROP and with experimental viscosity data from NIST ThermoData Engine #103b version 10.1, and the solid markers correspond to the fluids selected in Section 1. Dashed line for the critical point is given by $\sigma=0.6786(v_{\rm N,crit})^{1/3}$, for the triple point is given by $\sigma=(v_{\rm N,triple})^{1/3}$, and for the saturated liquid at $0.8T_{\rm c}$ is given by by $\sigma=0.8984(v_{\rm N,0.8T_c})^{1/3}$.

the experimental data scaled into simulation units. The largest value of $\eta^*/[(\rho^*)^{2/3}\sqrt{T^*}]$ available for the repulsive WCA potential is 4.3 for the highest density simulation run of (99). Therefore, the mapped data for $\eta^*/[(\rho^*)^{2/3}\sqrt{T^*}] > 4.3$ represent metastable extrapolation of the repulsive WCA results into the solid phase that should be considered with caution. 588

Finally, Fig. 8 presents a set of violin plots for all of the 580 experimental data for the full set of fluids in NIST REFPROP 590 with experimental viscosity data in NIST ThermoData Engine 59 #103b version 10.1. Nearly 50,000 experimental data points 592 are included in this collection. For each fluid, the optimized 593 value of σ for each fluid is used. In the recommended range of 594 validity of the WCA potential ($0.5 \leq -s^{\rm r}/R \leq 3.5$), 95% of the 595 data points are predicted within 18.1%, and the worst median 596 error is 4.2% for the bin at the largest value of $-s^{\rm r}/R$. The fully 597 predictive mode, where σ is taken from the correlation based 598 upon the volume of the saturated liquid at $0.8T_{\rm c}$, as described 599 in Fig. 7, results in a poorer representation of the experimental 600 viscosity, as shown in the SI Appendix. In predictive mode 601 and in the same range of validity, 95% of the data points are 602 predicted within 46.5%. 603

4. Conclusions and Outlook

This work has demonstrated that the Rosenfeld scaling of vis-605 cosity allows the viscosity of pure fluids and model potentials to 606 collapse to nearly monovariate functions of the residual entropy. 607 This monovariability allows for a mapping from molecular fluid 608 properties onto the properties of the model potentials for non-609 associating molecular fluids. Thus, a theoretically grounded 610 approach is demonstrated that connects model potentials and 611 molecular fluids through the residual entropy. The scaling 612 parameter σ is shown to be nearly proportional to measureable 613 length scales of the molecular fluids. 614

It is not conclusively shown that the WCA potential is the best possible model potential for the residual entropy corresponding states in viscosity; further study should consider whether other model potentials would be more suitable. For instance it is seen that the scaled viscosity data in Fig. 5 do not have the same curvature as the repulsive WCA potential.



Fig. 8. Violin plots of deviations in the prediction of viscosity with the optimized values of σ for each fluid for the mapping to the repulsive WCA reference potential for non-associating fluids. The range of $-s^r/R$ between 0.5 and 3.5 was split into bins of width 0.5. A violin distribution was constructed (by matplotlib(100)) for the results in each bin. The 97.5% and 2.5% percentiles are indicated with horizontal lines and the marker is the median value. Experimental data points for $-s^r/R$ greater than 3.5 or less than 0.5 are not shown, and in general correspond to much larger deviations.

A better potential would more faithfully represent the shape of the viscosity data in these scaled coordinates.

Ultimately, the connection between residual entropy and 623 viscosity stems from the fact that viscosity is primarily gov-624 erned by the repulsive interactions between molecules. The 625 structure in the fluid is driven by the repulsive interactions 626 (3, 77, 101), so if structure is the determinant of viscosity, and 627 if structure can be quantified by the residual entropy, then 628 it follows that the viscosity should be closely related to the 629 residual entropy. 630

There are many molecular fluids for which no experimental 631 viscosity data exist. This universal scaling approach, along 632 with the scaling parameters of Fig. 7, can yield a reasonable 633 estimate for viscosities of heretofore unmeasured fluids, as 634 long as they are not associating. Or, if a small number of 635 viscosity measurements are available, σ could be fit to those 636 data points and the entire liquid viscosity surface accurately 637 predicted within perhaps 20%. The mapping of associating 638 fluids onto model potentials remains a challenging endeavor, 639 and worth continued research effort. 640

641 Materials and Methods

The SI Appendix includes detailed information on the literature
data sources for each molecular fluid and model potential, mathematical derivations that complement the analysis in this manuscript,
as well as additional figures for completeness.

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